“Study of Molecular Interaction in Some Carbohydrates and Carbohydrate Polymers Using Spectroscopic Techniques”

A Synopsis Submitted to

Swami Ramanand Teerth Marathwada University, Nanded

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Doctor of Philosophy in Physics

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13.1. Introduction

Carbohydrates: the sugar molecules are one of the three main nutrients along with proteins and fats, found in foods and drinks. Our body breaks down carbohydrates into glucose which is the main source of energy for our body's cells, tissues, and organs. Glucose can be used immediately or stored in the liver and muscles for later use. Recently, 2-deoxy-d-glucose (2-DG) and glucose attracted many researchers due to their wide use in many diseases such as cancer, corona/covid-19 etc and other viral infections.

Though biological approach is different, but physical approach is equally important which are directly related to the biological applications that look into the structural and dynamical properties at atomic and molecular level that can be achieved by means of various spectroscopic techniques.

Spectroscopy method are very easy, accurate and appropriate to investigate structural and dynamical properties of materials in its pure or solvent environments. There are many types of spectroscopy techniques to investigate

1. Acoustic / Ultrasonic Spectroscopy
2. UV-Visible Spectroscopy
3. Fourier Transform Infra Red (FTIR) Spectroscopy
4. Dielectric Spectroscopy
5. Nuclear Magnetic Resonance (NMR) Spectroscopy

All these spectroscopic techniques explains various properties, structure and dynamics in the pure, binary, ternary or multi sample liquid mixtures etc.

1.4 Carbohydrates :

A carbohydrates is a biomolecules consisting of carbon(C), hydrogen(H) and oxygen(O) atoms, usually with a hydrogen-oxygen atom ratio of 2:1 (as in water) and thus with the empirical formula Cm(H2O)n (where m may or may not be different from n).

Carbohydrates are also known as saccharide, a group that include sugars, starch, and cellulose. The saccharides are divided into four chemical groups: Monosaccharides, disaccharides, oligosaccharides, and polysaccharides. Monosaccharides and disaccharides, the smallest (lower molecular weight) carbohydrates, are commonly refered to as sugars.

Carbohydrates performs numerous roles in living organisms. Polysaccharides serve for the storage of energy (e.g starch and glycogen) and as structural components (e,g cellulose in plants and chitih in arthropods). The 5-carbon monosaccharide ribose is an important component of coenzymes (e,g ATP,FAD and NAD)and the backbone of the genetic molecule known as RNA. The related deoxyribose is component of DNA.

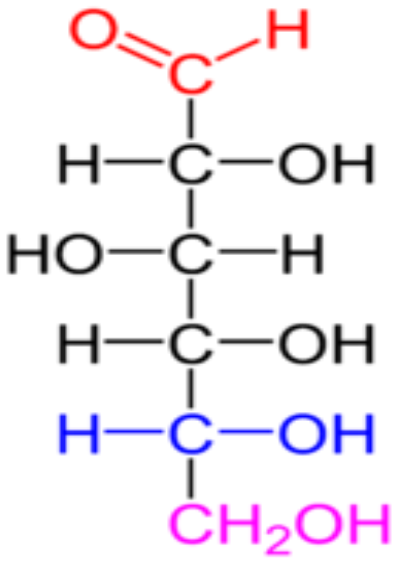


Fig : (a)

1.4 Types of Carbohydrates:

There are two types of carbohydrates Monosaccharides and Disaccharides.

Monosaccharides: Monosaccharides are the simplest carbohydrates in that they can not to hydrolyzed to smaller carbohydrate.

e.g Glucose and Fructose

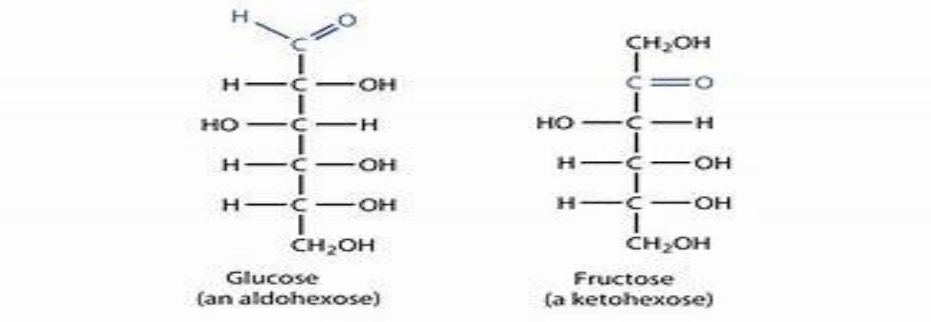


Fig : (b)

Disaccharides: A disaccharides is sugar formed when two monosaccharides are joined by glycosidic linkage.

e.g Sucrose, Lactose, Maltose

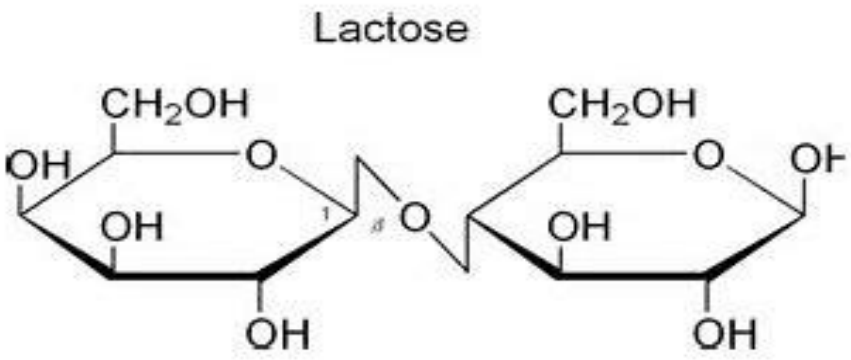


Fig : (c)

1.4 Carbohydrates Polymers:

A carbohydrate polymer is a string of sugar molecules linked together. It is also known as polysaccharides.

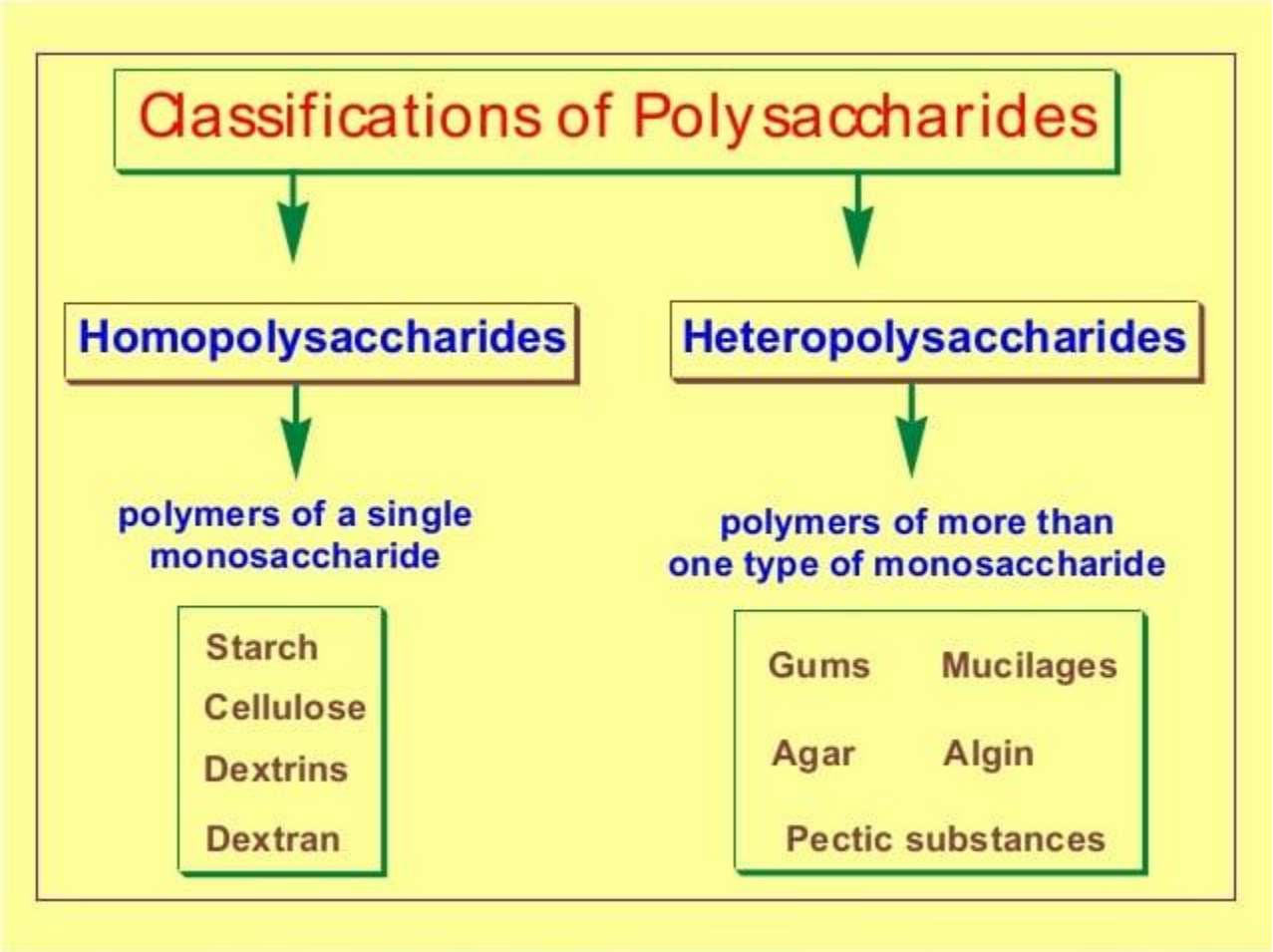

Classifications of Polysaccharides
Homopolysaccharides
Heteropolysaccharides
polymers of a single monosaccharide
polymers of more than one type of monosaccharide
Starch
Cellulose
Dextrins
Dextran
Gums
Mucilages
Agar
Algin
Pectic substances

Fig : (d)

2. Abstract of proposed work plan/ problem:

The proposed research work is aimed at the study of Molecular interaction in carbohydrates and some carbohydrates polymers at different concentrations and temperature using one of the spectroscopic techniques such as broad band dielectric spectroscopy, UV Visible , Raman, NMR, Acoustic spectroscopy etc.

The dielectric parameters such as complex dielectric spectra, dielectric constant, dielectric relaxation time and other thermodynamical properties such as enthalpy of activation, entropy of activation, free energy of activation are the key parameters to be investigated and studied in terms of hydrogen bonding and molecular interaction.

3. Review of Literature and Development in the subject (Previous work done in the relevant area):

There are several books and literature on carbohydrates and carbohydrates polymers and spectroscopic techniques available to understand the molecular behavior for the said systems [1,2,].

The reaction of the ester groups in pectin with alkaline hydroxylamine at room temperature produces hydroxamic acids. Pectin hydroxamic acid forms with ferric ions an insoluble complex and acetohydroxamic acid, produced from secondary acetyl groups of pectin, forms a soluble red complex. These reactions, applied to pectic substances, serve as the basis for a specific and rapid colorimetric method for the determination of up to 450 7 of acetyl per sample, with an accuracy within about ±2%. These reactions apply also to the quantitative determination of acetyl in acetylated carbohydrate polymers [3].

Recently, studies have been carried out on biodegradable chitosan/CNC composites with increased dielectric constant by modification of CNCs with –CN groups. Chemical modification has been probed in terms of FTIR and NMR, checking by XRD spectroscopy the presence of type I and II structures for cellulose and the small effect of chemical modification in the degree of crystallinity, as it probably occurred only at the surface of CNCs [4].

Photolithographic-defined films play an important role in modern optoelectronics and are crucial for the development of advanced organic thin-film transistros (OTFTs). The preparation of the cross-linked thin films of the subject materials followed by characterization of their dielectric properties. Next, OTFTs are fabricated demonstrating that the cross-linked cinnamate carbohydrate (cCin-Carb) films can be good gate dielectric materials. Finally, we explore the photopatterning characteristics of these materials demonstrating the superiority of the patterned cCin-Cellfilms for OTFT applications [5].

Dielectric permittivity and loss of a number of liquid and vitreous monosaccharides have been measured over arrange of frequencies from 100 to 105 Hz and temperature range -100 to 150 °C. In all cases either one or two relaxations were observed depending on the carbohydrate molecule; these occurred either just above the calorimetric 7g in the case of a single relaxation or both above and below 7g where two relaxations were observed. Fitting the relaxations to the Arrhenius on the monosaccharide [6].

The oxidation of aniline in acidic aqueous media using ammonium peroxydisulfate as oxidant has become the most widely used synthetic route to conducting PANi and is obtained as the protonated emeraldine salt (green color). It is deprotonated in alkalis to the corresponding emeraldine base, which is blue and non-conducting [7].

Water distribution and miscibility of carbohydrate and protein components in biological materials and their structural contributions in concentrated solids are poorly understood. In the present study, structural relaxations and a glass transition of protein hydration water and antiplasticization of the hydration water at low temperatures were measured using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) for bovine whey protein (BWP), aqueous glucose–fructose (GF), and their mixture [8].

The possibility of preparing first- and second generation furan derivatives, viz., a whole family of compounds derived from renewable resources, represents today a technological reality that opens the way to a variety of chemical processes. These operations range from the synthesis of high value-added compounds for drugs, fine chemicals, dyes, etc. to the preparation of macromolecular materials possessing very specific mechanical, optical, electronic, photochemical and eco logical properties based on the unique features associated with the furan heterocycle. The concept of a biomass refinery, capable of separating, modifying and exploiting the numerous constituents of renewable resources [9].

4. **Objectives of Research/ Proposed Hypothesis**:

The main objective of the proposed research work is to carry out and study molecular interaction, structural and dynamical behavior of some carbohydrates and carbohydrate polymers when environment of such systems i.e. temperature, concentration, number of atoms, frequency and other parameters changes. The effect of molecular weight, temperature and concentration on carbohydrates and carbohydrates polymers will also be the thrust areas of this work while studying molecular behavior and physical properties using different spectroscopic techniques [2,3].

4.2 Methodology to be adopted:

There are large number of techniques available to study the molecular interaction, structural and dynamical behavior of biomolecules and Polymers such as Fourier Transform Infra-Red (FTIR) [10-11,12] X-Ray[13], Nuclear Magnetic Resonance (NMR) [14] and Dielectric spectroscopy [15]. In the present work we will use some of these techniques to obtain information on the structural, dynamical and molecular interaction in Polymers/Biopolymers and biomolecules. Effect of concentration, frequency and temperature may also be included in the study.

Spectroscopic techniques gives vital information about structural dynamical properties of all kinds of liquids including organic, polymeric, biomolecules etc which can be useful for the development and other physical properties of substance under the study in pure as well as in aqueous form. In the present work we will use some of these techniques to obtain information on the structural, dynamical and molecular interaction in carbohydrates and carbohydrates polymers. Effect of concentration, frequency and temperature may also be included in the study.

4.2 Time Domain Reflectometry:

Time Domain Reflectometry (TDR) is used to describe a technique of observing time dependence reflection response of sample under study. H Fellner-Feldegg first developed it for measurement of loss and permittivity at very high frequency range. Time domain reflectometry is prepared to suitable fast rising pulse is applied to a transmission line, usually a co-axial line with 50Ω impedance. A co-axial line is connected to sampling device (sample holder). The schematic block diagram of the experimental setup for TDR is shown in Figure.

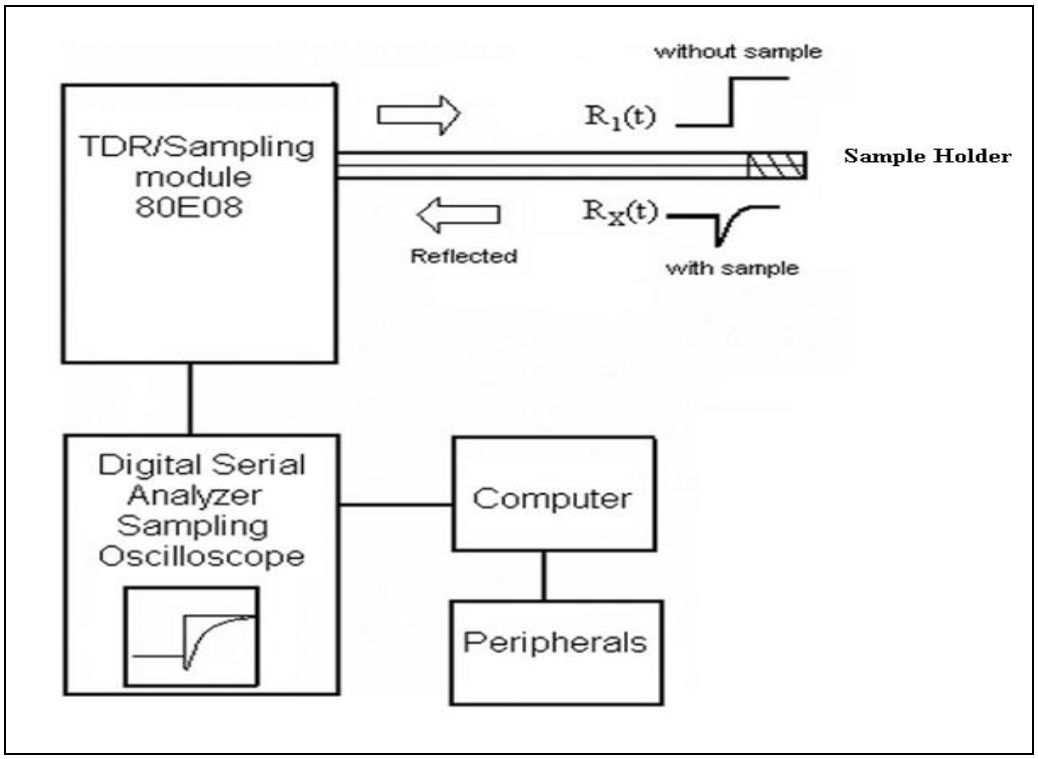


Fig.1: Schematic diagram of TDR.

In the basic TDR system a fast rising step voltage is propagated in an ideal coaxial line. The shape of step voltage remains unchanged as long as the propagation properties of the coaxial line remain the same. The complex permittivity of sample liquid is determined through Fourier transforming of the measured step pulses in the frequency range 10 MHz to 50 GHz.

4.2 Importance of study/ Society application:

- **International status/ National Status:**

Recently, due to wide band applications of carbohydrates and carbohydrates polymers in biological, pharmaceuticals and other industrial applications, Scientific community have attracted more to do in depth research on such biomolecules. Study on some green and benign

carbohydrate biopolymers and their derivatives for inhibition of metal corrosion have been carried out by ……[16]. Dielectric and electrical properties of Chitosan-hydroxyapatite composite materials have been carrier out by …[17]. The effect of water on the dielectric properties and electrical conductivity of thermoplastic starch (TPS) modified with microfibrillated cellulose and natural rubber latex microparticles was investigated using dielectric spectroscopy [18]. Temperature-dependent dielectric study have been obtained for all three main dispersion regions of lysozyme solutions in the frequency region 1 MHz to 40 GHz [19].

The ability of 2-deoxy-d-glucose (2-DG) to interfere with d-glucose metabolism demonstrates that nutrient and energy deprivation is an efficient tool to suppress cancer cell growth and survival. Acting as a d-glucose mimic, 2-DG inhibits glycolysis due to formation and intracellular accumulation of 2-deoxy-d-glucose-6-phosphate (2-DG6P), inhibiting the function of hexokinase and glucose-6-phosphate isomerase, and inducing cell death. In addition to glycolysis inhibition, other molecular processes are also affected by 2-DG. Attempts to improve 2-DG's drug-like properties, its role as a potential adjuvant for other chemotherapeutics, and novel 2-DG analogs as promising new anticancer agents are discussed in this review [20].

the complex dielectric constants of glucose solutions between 0.5 GHz and 12 THz (from the microwave to the far-infrared region) were measured in order to study peculiar anti-freezing and anti-dehydration properties point to a close association with their strong hydration capability and destructuring effect on the hydrogen bond (HB) network of bulk water [21].

Impedance spectroscopy was applied by Gilwon Yoon [22]. To determine glucose concentration in the interstitial fluid for its potential use in diabetic monitoring. For this purpose, the changes in

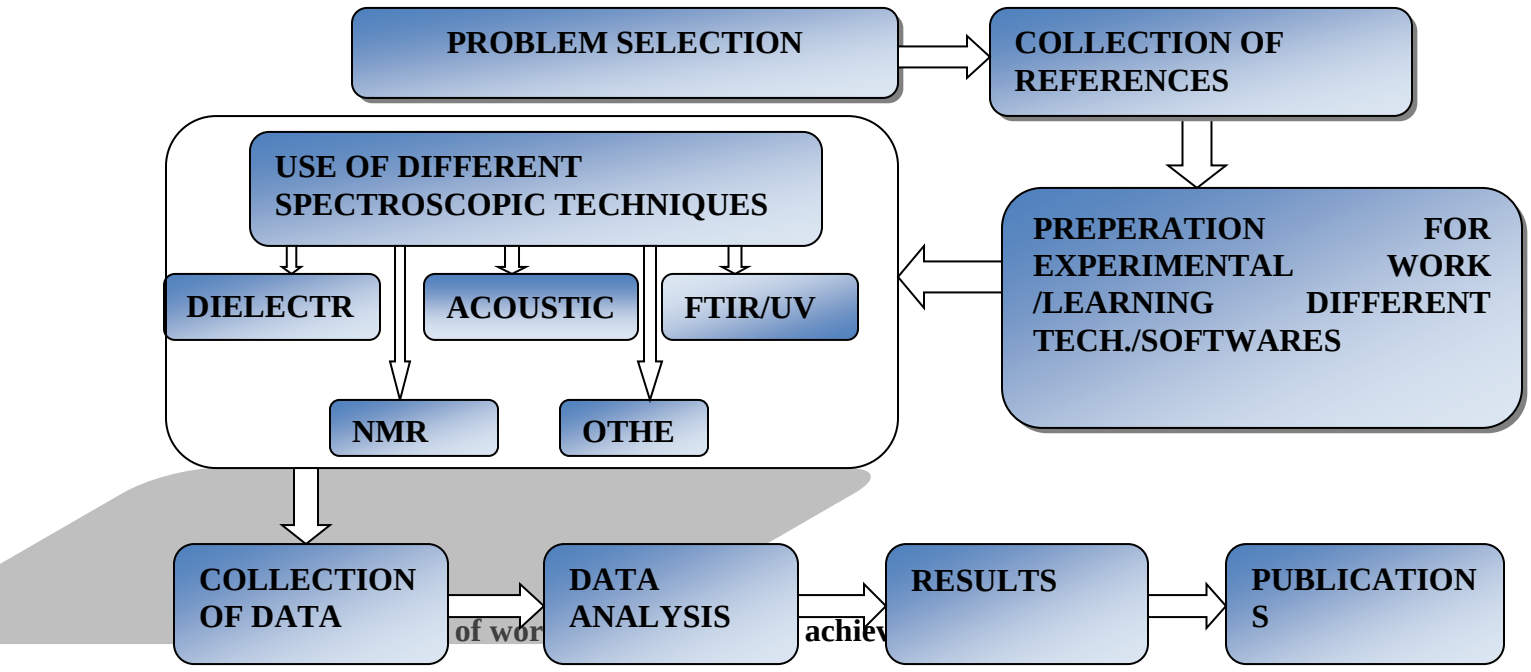
the measured dielectric properties due to the presence of glucose in water and saline solutions were examined between 40 Hz and 110 MHz.

5. Significance of the study :

Though many attempts have been carried out by scientist in order to study carbohydrates and carbohydrates polymer in all aspects. But broadband dielectric spectroscopy [BDS] in Time Domain Reflectometry [TDR] for carbohydrates and carbohydrates polymers gives in depth information at atomic and molecular level in terms of relaxation mechanism.

Through this work an attempt will be taken in order to study some of the carbohydrates which are recently in focused due to their wide band applications in the microwave frequency region at low temperature, in order to see the effect of temperature and concentration on the structural and dynamical properties of carbohydrates and carbohydrates polymers.

6. Proposed work Plan/ Formulation and Structure of Study:



Year/months	Target to be achieved
1-3 months	collection of References
4-9 months	Learning Different techniques
10-15 months	Experimental Work
16-21 months	Analysis
22-36 months	Project completion Report, Publication, Communication etc.

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